

MODIFIED ELECTRODE BASED ON ZEOLITE-ENCAPSULATED Cr(III) COMPLEX

Sara Gonçalves¹, Hugo Figueiredo², Bruna Silva², Teresa Tavares², Pier Parpot¹, Isabel C. Neves¹, António M. Fonseca¹, Anna E. Lewandowska³, Miguel A. Bañares³

¹*Departamento de Química, Universidade do Minho,*

Campus de Gualtar, 4170-057 Braga, Portugal - Email: ineves@quimica.uminho.pt

²*IBB – Instituto de Biotecnologia e Bioengenharia, Centro de Engenharia Biológica, Universidade do Minho, Campus de Gualtar, 4710-057, Braga, Portugal -*

Email: tavares@deb.uminho.pt

³*Instituto de Catálisis y Petroleoquímica, Instituto de Catálisis y Petroleoquímica, CSIC Universidad Autónoma de Madrid, E-28049-Madrid, Spain – Email: banares@icp.csic.es*

Zeolites are very important in materials science for the development of functional materials as well as in nanotechnology and these solids are very attractive in heterogeneous catalysis [1, 2]. For these applications, zeolites provide a rigid structure in which some active compounds can be included. In addition to the space constraints imposed by the zeolite, the negative charge of the zeolite framework and the distribution of the positive charges of the cations can lead to specific interactions with the zeolite framework which in turn induce structural and functional modifications as compared to solution activities [2].

The first syntheses of encapsulated complexes within zeolites generated much interest due to effects of site isolation and steric confinement on the physical properties and chemical reactivity of the molecules trapped within supercages of the crystalline microporous zeolite lattice [3]. Zeolite-encapsulated transition metal complexes are generally characterized by spectroscopic techniques and elemental analyses [4].

This work reports the studies of the electrochemical behaviour of Cr(III)-PAN complexes encapsulated in NaY zeolite. The redox properties of these zeolite-encapsulated complexes were investigated by cyclic voltammetry with a new method for the preparation of carbon toray-zeolite-modified electrode.

The synthesis of Cr(III) complexes encapsulated in supercages of Y zeolite was carried out by free diffusion of the PAN (1-(2-pyridylazo)-2-naphtol) ligand (Figure 1) through the zeolite pores exchanged with the Cr(III) metal ion, obtained by the previous use of the biosorption process [5].

The resulting materials were characterized via surface analysis (SEM, XRD), chemical analysis, spectroscopic methods (FTIR and Raman) and cyclic voltammetry in aqueous medium with zeolite-modified electrodes.



Figure 1 – 1-(2-pyridylazo)-2-naphtol (PAN) ligand

Zeolite-encapsulated Cr(III)-PAN complex was deposited on carbon Toray (CT) in order to determine the electroactivity by cyclic voltammetry. The cyclic voltammetry studies obtained with a new method for the preparation of zeolite-modified electrodes shows

evidence for electroactivity restricted to boundary associated Cr(III)-PAN complexes (Figure 2).

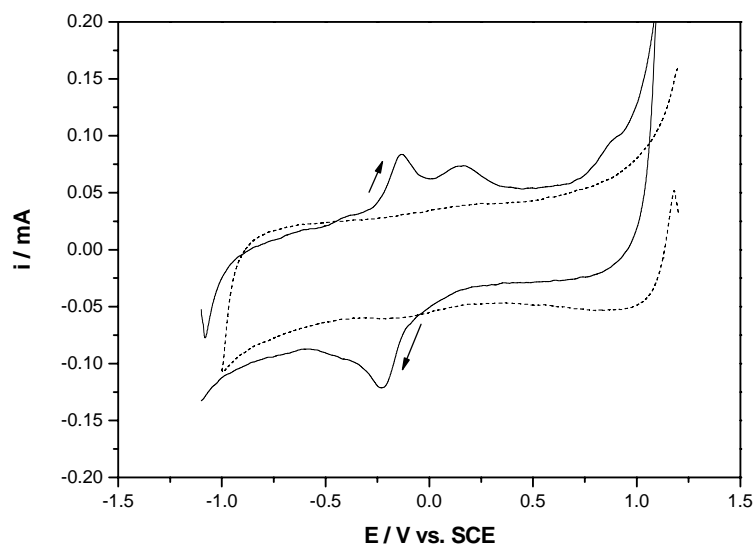


Figure 2 - The voltammograms of Cr(III)PAN-NaY/Carbon (.....) and Cr(III)PAN-NaY/Carbon (—) in 0.1 M NaCl at ambient temperature (scan rate: 50 mV s⁻¹)

The combination of the spectroscopic techniques and elemental analysis with electrochemical methods provide a powerful tool to reveal the unequivocal evidence for the encapsulation of Cr(III)-PAN complex in the supercages of zeolite Y. The micro Raman spectra underline a non-homogeneous distribution of chromium oxide species. Figure 3a shows the Raman spectrum at spots that exhibit orange color in optical microscopy while Figure 3b, that of the white spots. The Raman bands 1001 and 882 cm⁻¹ are related to surface chromium (VI) oxide species (Fig. 3a). A band at 880 cm⁻¹ is attributed to the stretching mode of bridging oxygen sites (Cr-O-Cr) in surface polymeric Cr^{VI} species. The 1001 cm⁻¹ Raman band is assigned to the terminal Cr=O stretching mode in surface isolated and polymeric Cr^{VI} species. The Raman spectra show no Cr₂O₃ aggregates, which would exhibit an intense band at 550 cm⁻¹.

The bands observed on the Raman spectrum, Figure 3b, are assigned to NaY zeolites vibration modes. The Raman bands observed between 200 and 600 cm⁻¹ are assigned to the motion of the oxygen atom in a plane perpendicular to the T-O-T bonds in the zeolite structure.

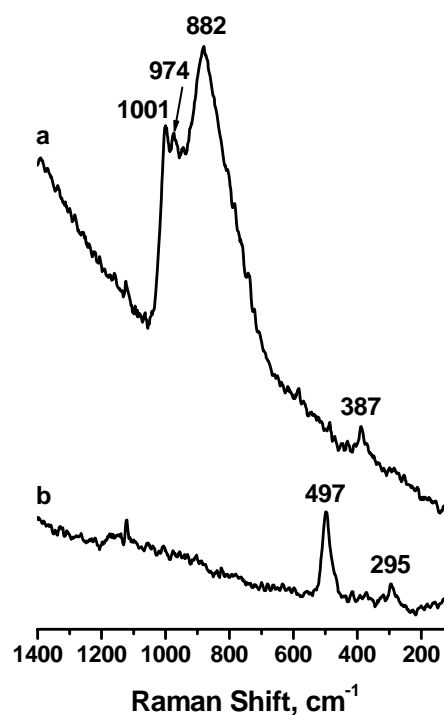


Figure 3 – Raman spectra of dehydrated Cr-NaY catalyst.

References:

- [1] M. E. Davis, *Nature*, **417** (2002) 813-821.
- [2] A. Corma, H. Garcia, *Eur. J. Inorg. Chem.*, **6** (2004) 1143-1164.
- [3] C.A. Bessel, D. Rolison, *J. Phys. Chem. B*, **101** (1997) 1148-1157.
- [4] F. Costa, C.J.R. Silva, M.M.M. Raposo, A.M. Fonseca, I.C. Neves, A.P. Carvalho, J. Pires, *Microporous Mesoporous Mater.*, **72** (2004) 111-118.
- [5] H. Figueiredo, I.C. Neves, C. Quintelas, T. Tavares, M. Taralunga, J. Mijoin, P. Magnoux, *Appl. Catal. B: Environmental*, **66** (3-4) (2006) 274-280.